Indian Journal of Chemistry
Vol. 14A, February 1976, pp. 78-81

Kinetics & Mechanism of Anation of Aquopentaamminecobalt(III) by Carboxylate Ligands: Mechanism of Formation of Phthalatopentaamminecobalt(III) Complex

A. C. DASH* & NITYANANDA RAY†
Department of Chemistry, Utkal University, Bhubaneswar 4

Received 18 *November* 1974; *accepted* 3 *April* 1975

Anation of aquopentaamminecobalt(III) by *o*-phthalate ions, HPh^- and Ph^{2-}, has been studied in a medium of 0·3*M* ionic strength and at 50, 55 and 60°. The observed pseudo-first order rate constants obey the rate law

$$k_{obs} = \frac{k_1Q_1[HPh^-]+k_2Q_2[Ph^{2-}]}{1+Q_1[HPh^-]+Q_2[Ph^{2-}]}$$

where Q_1, k_1 and Q_2, k_2 represent the stability constant and outersphere-innersphere interconversion rate constant of the ion-pairs, $[(NH_3)_5CoOH_2]^{3+}.HPh^-$ and $[(NH_3)_5CoOH_2]^{3+}.Ph^{2-}$, respectively. At 60° the values of k_1, Q_1 and k_2, Q_2 are found to be $2{\cdot}88(\pm0{\cdot}07)\times10^{-4}$ sec^{-1}, $2{\cdot}92(\pm0{\cdot}42)M^{-1}$ and $3{\cdot}73(\pm0{\cdot}37)\times10^{-4}$ sec^{-1}, $30{\cdot}0(\pm6{\cdot}0)M^{-1}$ respectively. The activation enthalpy and entropy for the interchange reaction of the HPh^- and Ph^{2-} ion-pairs are $28{\cdot}4(\pm0{\cdot}8)$ kcal mole^{-1}, $10{\cdot}3(\pm2{\cdot}4)$ cal deg^{-1} mole^{-1} and $24{\cdot}5(\pm2{\cdot}8)$ kcal mole^{-1}, $-0{\cdot}7(\pm8{\cdot}0)$ cal deg^{-1} mole^{-1} respectively. It is suggested that the formation of phthalatopentaamminecobalt(III) complex from ion-pairs involves water dissociation from the cobalt (III) centre as the rate limiting step. The observed reactivity sequence, $k_2>k_1$ of the ion pairs may be taken to be an evidence of stronger labilizing action of Ph^{2-} ion compared to HPh^- on the coordinated water molecule.

THE replacement of water from the aquopentaamminecobalt(III) ion by anionic nucieophiles is believed to involve ion-association equilibria between the reacting species. This is followed by the interchange of the coordinated water molecule with the ion-pairing anion. Earlier studies[1] have indicated that the dissociative interchange mechanism most likely operates in the anation reactions of $[(NH_3)_5CoOH_2]^{3+}$ with the anions like Cl^-, Br^-, NO_3^-, NCS^-, SO_4^{2-} and $H_2PO_4^-$. The reactant association-water dissociation mechanism also appears to be applicable in the anation reactions of $[(en)_2Co(OH_2)_2]^{3+}$ with sulphate[2], phosphate[3], and oxalate[4]. Study of the formation of the carboxylatopentaamminecobalt(III) complexes offers another interesting possibility for examining the dissociative interchange mechanism in cobalt(III) system. Furthermore the study of the mechanism of anation of $[(NH_3)_5CoOH_2]^{3+}$ by carboxylate ligands is expected to throw light into the mechanism of spontaneous aquation of carboxylatopentaamminecobalt(III) complexes[5]. It was, therefore, thought worthwhile to attempt a systematic study of the mechanism of formation of carboxylatopentaamminecobalt(III) complexes which have been very sparingly investigated so far[6]. The present work describes the kinetics and mechanism of formation of *o*-phthalatopentaamminecobalt(III) ion. The reaction has been studied in aqueous phthalate buffer medium at 50°, 55° and 60° and $\mu = 0{\cdot}3M$ ($NaClO_4$).

Materials and Methods

Aquopentaamminecobalt(III) perchlorate, $[(NH_3)_5CoOH_2](ClO_4)_3$ was prepared and purified by the method of Harris *et al.*[7] (Found: Co, 12·79. Reqd: Co, 12·70%). The molar extinction coefficients of $[(NH_3)_5CoOH_2]^{3+}$ measured in $0{\cdot}1M$ $HClO_4$ compared satisfactorily with the same reported by Harris *et al.*[7] in the range of wavelength 340-600 nm. *o*-Phthalatopentaamminecobalt(III) perchlorate $[(NH_3)_5CoCO_2C_6H_4CO_2H](ClO_4)_2$ was prepared by the method of Gould and Taube[8]. (Found: Co, 11·6. Reqd: Co, 11·4%). The phthalato complex exhibits the two band spectrum in $0{\cdot}05M$ $HClO_4$ medium centred around 350 and 500 nm. The molar absorbancy indices of $[(NH_3)_5CoCO_2C_6H_4CO_2H]^{2+}$ ion were found to be 77·2 (±1·0), 78·6 (±0·8), and 76·5 (±0·8)M^{-1} cm^{-1} at 500, 510 and 350 nm respectively. The molar extinction coefficient of the above complex has been reported by Gould and Taube[8] to be $79{\cdot}5M^{-1}$ cm^{-1} at 503 nm.

o-Phthalic acid (E. Merck, extrapure) sodium hydroxide (BDH, AR) perchloric acid (Baker analysed) and sodium perchlorate (Reidel) were used. The standard solutions of sodium hydrogenphthalate and sodium phthalate were prepared by dissolving a known amount of phthalic acid in a standard solution of sodium hydroxide. Potassium hydrogenphthalate (AR) was used to standardize alkali. All solutions were prepared in distilled water freshly received from a copper still.

Kinetic measurement — Solutions of desired composition were prepared in 100 ml measuring flasks and equilibrated in the thermostat. A known

*To whom all correspondence may be directed.
†Present address: Department of Chemistry, Bhadrak College, Bhadrak.

weight of aquopentaamminecobalt(III) perchlorate was transferred into the reaction flask. The complex dissolved on shaking and the volume was made up with distilled water at the reaction temperature. The progress of the reaction was followed by withdrawing aliquots of the reaction mixture at definite time intervals, cooling down to room temperature and then measuring optical density at 500 and 510 nm. A Beckmann DU 2 spectrophotometer with 1·0 cm matched silica cell was used for all spectral measurements. The observed pseudo-first order rate constants for anation reaction were obtained from the slope of the linear plot of ln $(D_\infty - D_t)$ versus time where D_t and D_∞ stand for the optical density of the reaction mixture at time t and for the complete anation of the aquo complex respectively. D_∞ for any run was computed from the concentration of aquo complex and the extinction coefficient of the phthalatopentaamminecobalt(III) complex. Interference due to aquation of the product [i.e. phthalatopentaamminecobalt(III)] in the percentage of reaction from which the rate constants were isolated was found to be negligible.

Results

Anation of aquopentaamminecobalt(III) ion with *o*-phthalate results in the formation of phthalatopentaamminecobalt(III) complex with no other side product. This is evidenced from the close correspondence between the spectrum of phthalatopentaamminecobalt(III) and that of the reaction mixture at infinite time for a few runs at 60° in which $[HPh^-]$ was $0{\cdot}08M$. The pseudo-first order rate constants (k_{obs}) for the anation reaction at 50-60° and under varying concentration of phthalic acid, hydrogen phthalate, and phthalate are presented in Table 1. k_{obs} is found to be independent of [phthalic acid] in the range studied. k_{obs}, however, increases with the increase in $[HPh^-]$ and $[Ph^{2-}]$. Both $k_{obs}/[HPh^-]$ and $k_{obs}/[Ph^{2-}]$ at a given $[HPh^-]$, decrease with $[HPh^-]$ and $[Ph^{2-}]$ respectively. This is reconciled with the fact that the rate limiting step involved in the anation process is preceded by reactant association. Taking this into account, the various steps for the reaction under study may be depicted as follows:

$$(NH_3)_5CoOH_2^{3+} + HPh^- \overset{Q_1}{\rightleftharpoons} [(NH_3)_5CoOH_2.HPh]^{2+} \xrightarrow{k_1} (NH_3)_5CoHPh^{2+} + H_2O$$

$$(NH_3)_5CoOH_2^{3+} + Ph^{2-} \overset{Q_2}{\rightleftharpoons} [(NH_3)_5CoOH_2.Ph]^{+} \xrightarrow{k_2} (NH_3)_5CoPh^{+} + H_2O.$$

According to such a scheme k_{obs} will have the form:

$$k_{obs} = \frac{k_1Q_1[HPh^-] + k_2Q_2[Ph^{2-}]}{1 + Q_1[HPh^-] + Q_2[Ph^{2-}]} \qquad \ldots(1)$$

The pseudo-first order rate constants at $[Ph^{2-}] = 0$ and $[HPh^-] = 0{\cdot}02\text{-}0{\cdot}2M$ were fitted to the relationship, $k_{obs} = k_1Q_1[HPh_1]/(1 + Q_1[HPh^-])$, derived from Eq. (1), by means of a computer programme adopted to IBM 1130 computer. With the input values of k_1Q_1 and Q_1 obtained from the linear plots of $1/k_{obs}$ versus $1/[HPh^-]$ the programme varied these parameters and minimized the sum of the weighted residuals $\Sigma[(k_{calc} - k_{obs})/\sigma(k_{obs})]^2$. With the least squares best values of k_1Q_1 and Q_1, the rate constants (k_{obs}) at $[HPh^-] = 0{\cdot}1M$ and $[Ph^{2-}] = 0\text{-}0{\cdot}06M$ were fitted to Eq. (1) by the weighted least squares procedure to get the parameters k_2Q_2 and Q_2. The approximate values of k_2Q_2 and Q_2 which were used in this calculation were obtained from the linear plots of $1/(k_{obs} - k'_{obs})$ versus $1/[Ph^{2-}]$ where $k_{obs} = k'_{obs}$ at $[Ph^{2-}] = 0$, $[HPh^-] = 0{\cdot}1M$ and $[H_2Ph] = 0{\cdot}01M$. The calculated values of the parameters of Eq. (1) at different temperatures have been collected in Table 1. These values of the parameters reproduce the pseudo-first order rate constants within the experimental error (see k_{calc} in Table 1). Thus it is evident that the rate data fit the proposed mechanism well.

The ion-pair rate constants (k_1, k_2) were fitted to the transition state equation $k = (RT/Nh) \exp(-\Delta H^*/RT + \Delta S^*/R)$, by the weighted least squares procedure mentioned earlier. The enthalpy and entropy change associated with the formation of the ion-pairs have been calculated from the relationship $\ln Q = -\Delta H/RT + \Delta S/R$, taking account of the error of Q. The activation parameters for the anation reaction and the enthalpy and entropy changes associated with the formation of the ion-pairs have been collected in Table 2.

Discussion

It is observed that phthalic acid in the concentration range $0{\cdot}002\text{-}0{\cdot}04M$ does not form an outer sphere complex with aquopentaamminecobalt(III) ion and also the latter does not undergo anation by the former. This is in contrast to the observations recorded by Brown and Harris[4] in their study on the kinetics of anation of *cis*-diaquobis-(ethylenediamine)cobalt(III) by oxalic acid. This may be due to the fact that the hydrogen bonding effect which is primarily responsible for the association of H_2Ph with $[(NH_3)_5CoOH_2]^{3+}$ and $H_2C_2O_4$ with $[(en)_2Co(OH_2)_2]^{3+}$ is more pronounced for the latter than for the former system. Furthermore the experimental conditions employed by Brown and Harris are widely different from those of ours. Probably it is necessary to work at relatively high concentration of H_2Ph to understand the mechanism and anation rate profile of aquopentaamminecobalt (III) by such a species. This could not be done beyond $[H_2Ph] > 0{\cdot}04M$ due to the limited solubility of phthalic acid.

The aquo complex under study is found to undergo anation via the formation of the reactive ion-pairs with HPh^- and Ph^{2-}. The formation of HPh^- ion-pair is associated with low and negative enthalpy and entropy changes. On the other hand the association of Ph^{2-} with $[(NH_3)_5CoOH_2]^{3+}$ results in endothermic heat change and significantly large positive entropy change (see Table 2). The negative value of $\Delta S(Q_1)$ is consistent with the decrease of the number of ions in the formation of HPh^- ion-pair. The high positive value of $\Delta S(Q_2)$, however, points out that the entropy loss due to the association of Ph^{2-} with $[(NH_3)_5CoOH_2]^{3+}$ is more than counter-balanced by the desolvation of the associating ions and much less solvation of the phthalate

TABLE 1 — DATA FOR THE ANATION OF AQUOPENTAAMMINECOBALT(III) BY HPh^- AND Ph^{2-}

{Ionic strength = 0·3M, $[(NH_3)_5CoOH_2^{3+}] = (5{\cdot}1\text{-}8{\cdot}7)\times10^{-3}M$}

$[H_2Ph]$ (M)	$[HPh]$ (M)	$[Ph^{2-}]$ (M)	$k\times10^6$ sec^{-1} at* 50° Obs.	50° Calc.	55° Obs.	55° Calc.	60° Obs.	60° Calc.
0·002	0·02		4·67 (±0·18)	4·54	8·64 (±0·29)	8·68	15·9 (±0·4)	15·9
0·01	0·02		4·64 (±0·15)	4·54	8·54 (±0·18)	8·68	16·4 (±0·6)	15·9
0·02	0·02		4·58 (±0·16)	4·54	8·58 (±0·21)	8·68	16·2 (±0·4)	15·9
0·04	0·02		4·63 (±0·10)	4·54	8·62 (±0·17)	8·68	15·5 (±0·5)	15·9
0·004	0·04		8·39 (±0·23)	8·54	16·5 (±0·4)	16·4	30·1 (±0·5)	30·1
0·006	0·06		12·0 (±0·6)	12·1	23·3 (±0·4)	23·4	43·1 (±0·6)	42·9
0·008	0·08		15·6 (±0·7)	15·3	29·5 (±0·8)	29·7	54·0 (±1·0)	54·5
0·01	0·1		18·2 (±0·5)	18·2	35·7 (±0·7)	35·3	65·1 (±1·3)	65·0
0·02	0·2		29·2 (±0·8)	29·2	57·2 (±1·2)	57·4	109·0 (±8·0)	106·0
	0·1	0·01	32·7 (±1·0)	32·2	62·5 (±1·0)	62·4	125·0 (±5·0)	123·0
	0·1	0·02	42·1 (±1·2)	42·6	80·9 (±3·0)	82·1	163·0 (±3·0)	163·0
	0·1	0·04	57·1 (±1·1)	57·2	110·0 (±4·0)	109·0	209·0 (±8·0)	214·0
	0·1	0·06	67·0 (±1·2)	66·8	127·0 (±4·0)	127·0	250·0 (±10·0)	245·0
$k_1Q_1\times10^4$, sec^{-1} M^{-1}			2·42 (± 0·07)		4·60 (±0·09)		8·41 (±0·19)	
Q_1, M^{-1}			3·28 (±0·38)		3·02 (±0·28)		2·92 (±0·42)	
$k_1\times10^5$, sec^{-1}†			7·38 (±0·21)		15·2 (±0·3)		28·8 (±0·7)	
$k_2Q_2\times10^4$, sec^{-1} M^{-1}			25·8 (±2·2)		49·9 (±3·3)		112·0 (±11·0)	
Q_2, M^{-1}			22·5 (±3·7)		23·6 (±3·5)		30·0 (±6·0)	
$k_2\times10^4$, sec^{-1}†			1·15 (±0·10)		2·11 (±0·14)		3·73 (±0·37)	

*k_{obs} was calculated from 15 to 75% of reaction. Each entry for k_{obs} is based on four to six determinations.
†$\sigma(k) = \sigma(kQ)/Q$.

TABLE 2 — THERMODYNAMIC PARAMETERS FOR THE FORMATION OF THE ION-PAIRS AND THE ACTIVATION PARAMETERS FOR THEIR ANATION REACTION

(Ionic strength = 0·3M)

	k_1 path	k_2 path
ΔH^* (kcal mole^{-1})	28·4 (±0·8)	24·5 (±2·8)
ΔS^* (cal deg^{-1} mole^{-1})	10·3 (±2·4)	−0·7 (±8·0)

$\Delta H(Q_1) = -2{\cdot}6$ (±0·7) kcal mole^{-1}; $\Delta H(Q_2) = 5{\cdot}7$ (±2·7) kcal mole^{-1}
$\Delta S(Q_1) = -5{\cdot}7$ (±2·1) cal deg^{-1} mole^{-1}; $\Delta S(Q_2) = 23{\cdot}9$ (±8·3) cal deg^{-1} mole^{-1}

ion-pair relative to that of hydrogenphthalate analogue. The average values of the stability constants of the HPh^- and Ph^{2-} ion-pairs range from 3·28 to 2·92 and 22·5 to 30·0 respectively in the temperature interval 50-60° and 0·3M ionic strength. The reliability of the experimental values of Q may be checked by calculating the stability constants of the ion-pairs from the coulombic force concept. On the basis of the hard sphere model[9] the calculated values of Q_1 and Q_2 at 50° (μ = 0·3M) turn out to be 3·18M^{-1} and 18·6M^{-1} respectively in fair agreement with the experimental data when the distance of the closest approach* of the associating ions is taken to be 6 Å. Thus the above calculation provides support for the proposed reactant association mechanism for the anation of $[(NH_3)_5CoOH_2]^{3+}$ with the phthalate species.

*The distance of closest approach was assumed to be 6Å in computing the stability constant of the ion-pair of $(en)_2Co(OH_2)_2^{3+}$ with $C_2O_4H^-$ (see ref. 4).

The activation enthalpy and entropy associated with the inter-conversion of the HPh^- and Ph^{2-} ion-pairs to the corresponding phthalatopentaamminecobalt(III) species are 28·4 (±0·8) kcal/mole, 10·3 (±2·4) cal deg^{-1} mole^{-1} and 24·5 (±2·8) kcal/mole, −0·7 (±8·0) cal deg^{-1} mole^{-1} respectively. [The activation parameters for the water exchange reaction[10] of $(NH_3)_5CoOH_2^{3+}$ are ($\Delta H^* = 27$ kcal/mole and $\Delta S^* = 6$ cal deg^{-1} mole^{-1})].

The rate constants for the interchange reactions of the HPh^- and Ph^{2-} ion-pairs, calculated from the activation parameter data, are $1{\cdot}7\times10^{-6}$ sec^{-1} and $4{\cdot}3\times10^{-6}$ sec^{-1} respectively at 25°. These are in fair agreement with the analogous rate data for CNS^-, SO_4^{2-}, and $H_2PO_4^-$ ion-pairs of aquopentaamminecobalt(III) and water exchange rate constant for the latter at 25° and 0·5M ionic strength (10^6 k_{int}, sec^{-1} = 0·29 for CNS^-, 1·3 for SO_4^{2-}, 0·73 for $H_2PO_4^-$, 6·6 for H_2O)[11]. Thus it appears from the consideration of the rate and activation parameters that the outersphere-innersphere interconversion process for the phthalate ion-pairs is governed by the rate limiting water dissociation from the cobalt(III) centre. It is, however, important to note that the Ph^{2-} ion-pair reacts faster than its HPh^- analogue ($k_2 \simeq 1{\cdot}5k_1$ at 50-60°). This sequence of the reactivities of the ion-pairs when rationalized on the basis of the proposed dissociative interchange mechanism points to the fact that Ph^{2-} ion exerts stronger labilizing action on the coordinated water molecule than HPh^-. The hydrogen bonding interaction of the leaving water molecule with the carboxylate group and electrostatic as well as steric repulsion between the negative end of the water dipole and the carboxylate group in the transition state of the interchange process of the Ph^{2-} ion-pair

may be some of the factors which govern the labilizing action of Ph^{2-} ion mentioned above. Further work on similar system is in progress to understand this aspect of the problem.

Acknowledgement

The authors are thankful to Dr R. K. Nanda, Department of Chemistry, Utkal University, for his interest in this work.

References

1. Basolo, F. & Pearson, R. G., *Mechanisms of inorganic reactions* (Wiley, New York), 1967.
2. Barraclough, C. G. & Murray, R. S., *J. chem. Soc.*, (1965), 7047.
3. Lincoln, S. F., Murray, R. S. & Stranks, D. R., *Proceedings of the 9th international conference on coordination chemistry* (St Moritz, Switzerland), Sept. 1966, 357.
4. Brown, P. M. & Harris, G. M., *Inorg. Chem.*, **7** (1968), 1872.
5. Haim, A., *Inorg. Chem.*, **9** (1970), 426.
6. Banerjea, D. & Roy, J., *Z. anorg. allg. Chem.*, **400** (1973), 89.
7. Splinter, R. C., Harris, S. J. & Tobias, R. S., *Inorg. Chem.*, **7** (1968), 898.
8. Gould, E. S. & Taube, H., *J. Am. chem. Soc.*, **86** (1964), 1318.
9. Hammes, G. G. & Steinfeld, J. I., *J. Am. chem. Soc.*, **84** (1962), 4639.
10. Basolo, F. & Pearson, R. G., *Mechanisms of inorganic reactions* (Wiley, New York), 1967, 164.
11. Basolo, F. & Pearson, R. G., *Mechanisms of inorganic reactions* (Wiley, New York), 1967, 203.